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Metallic spin-glasses beyond mean-field theory: An approach to the impurity-concentration dependence of the freezing temperature

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A relation between the freezing temperature (T_g), and the concentration of spins in metallic spin-glasses is presented, where T_g is obtained as a weighted sum of the absolute values of the spin-spin couplings, taking the critical scaling of the correlation function into account. Interestingly, we find that no disorder-average is required. We compare our theoretical predictions with experiments and find good agreement with the available data from *Cu*Mn, *Ag*Mn, and *Au*Fe alloys.

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The relationship between the freezing temperature (T_g), the distribution of spin-spin couplings (K_{ij}), and the concentration of impurities (c) in metallic spin-glasses has been the subject of vigorous research [1–5]. Mean-field(MF)-based analytical approaches in ref.[3, 4] showed $T_g \sim \sqrt{\sum_{j\neq i}[K_{ij}^2]_{\rm av}}$ (where $[\cdot]_{\rm av}$ denotes the average over configurations of the disorder). Despite predicting the correct low concentration limit $T_g \propto c$, this formula does not fit the experiments well[5]. A different phenomenological relation $T_g \sim \sum_{j\neq i}\sqrt{[K_{ij}^2]_{\rm av}}$ was derived in ref.[5], and an overall good fit to the experiments was obtained at moderate c. However, the latter does not reproduce the asymptotic linear behavior in the low concentration limit. We derive in this Letter an alternative equation for T_g that takes the statistical properties of the correlations into account, and fits the experimental findings well.

The system: We will be looking at magnetic impurities (Fe, Mn), the spins, diluted ($0.05\ \% \lesssim c \lesssim 7\ \%$) in a noble metal (Au, Ag, Cu). At such low concentrations, the spins interact mainly by means of the conduction electrons; i.e., through the RKKY interaction[6] $K_{ij} \propto r_{ij}^{-3}\cos(2k_{\rm F}r_{ij})$, where $k_{\rm F}$ is the Fermi wavevector, and r_{ij} is the distance between the spins. The quenched positional disorder, together with the strongly oscillating sign of K_{ij}, results in an even distribution of couplings, with zero as dominant mean[1, 2]. Such a distribution leads to frustration, and to the formation of the spin-glass phase. In this low temperature phase (for $T < T_g$), the spins are frozen in "random" orientations, without a conventional long-range order. In average, about half of the spins freezes, with their relative orientations trying to satisfy the signs of the pairwise interactions, whereas the other half is frustrated [1, 2, 7]. Two alloys with equal concentration of impurities show identical behavior; meaning that the macroscopic state is insensitive to the differences among the configurations of the microscopic disorder[1, 2, 5, 7].

The solution: Let us start, considering the spin system in the paramagnetic phase, where the thermal average of every spin $\langle S_i\rangle$ is zero. Let S_0 be a test spin, which we presume has a non vanishing thermal average $\langle S_0\rangle = \delta S_0$. This would change the local fields by $\delta h_j = K_{j0}\delta S_0$. δh_j would affect the neighboring spins, and these, their neighbors, and so on. According to the linear-response theory, this far-reaching effect is given, at any point, in terms of the spin-spin correlations $G_{ij} \equiv \langle S_i S_j\rangle$, as $\delta S_i = \beta\sum_j G_{ij}\delta h_j$, with $\beta = T^{-1}$. Now we relax the constraint of S_0 having an "externally" fixed thermal average, and ask ourselves whether δS_0 can be maintained by the self-induced local fields. If yes, this would imply that the paramagnetic phase is unstable, which takes place when

$$\beta\sum_j G_{0j}K_{j0} = 1\ . \tag{1}$$

More generally, we must consider the effect on all spins, starting by variations at an arbitrary number of sites. Doing so, we obtain that the paramagnetic phase is unstable when an eigenvalue $\epsilon_{\rm Max}$ of $Q \equiv \beta GK$ equals one; i.e.,

$$\mathrm{Max}(\epsilon[Q]) = 1\ . \tag{2}$$

Eq.(2) gives the temperature at which the spins acquire a non vanishing thermal average as a consequence of their site-to-site correlations. It holds for spin-glasses, as well as for ferromagnets. The specific type of order is determined by the actual distribution of K_{ij}, which also determines the functional form of G_{ij}. MF-based approaches[3, 4, 8], or perturbation expansions[9] are alternatives to avoid the unknown exact form of G_{ij}, by setting $G_{ij} \equiv \delta_{ij}$ at the start, and trying to recover fluctuations/correlations or introducing reaction fields, at a later stage. We proceed here in a different way, and stay with Eq.(2). As the long range of the RKKY interaction is essential to the glass phase in diluted metallic alloys[1, 2, 5], a detailed knowledge of the correlations between a spin and its nearest neighbors is neither necessary nor sufficient. We rather look for the general behavior of G_{ij} over the whole interaction range.

Solving Eq.(2) seems a formidable problem, but we will show now that it leads us back to Eq.(1). As a

consequence of the disorder, neither G_{ij} nor K_{ji} is a self-averaging quantity. The bonds K_{ji} are uncorrelated from each other, and the products $G_{ij}K_{jl}$ are weakly correlated. Every matrix element $Q_{il} \equiv \beta \sum_j G_{ij}K_{jl}$, being defined as a sum over all $N-1$ sites ($j \neq l$), samples many different K_{jl}, covering the whole range of the distribution. Then, that Q_{il} is a scalar matrix, and thus self-averaging, follows from the theory of large deviations[10]. For $i \neq l$, G_{ij} and K_{jl} correspond to different pairs; the product $G_{ij}K_{jl}$ can be either negative or positive with equal probability. Then, the sum over j, and therefore Q_{il}, converges to zero. For $i = l$, the sum is greater than zero, because G_{ij} follows the sign of K_{ji} as long as the frustration allows it, and only about half of the system is frustrated[1, 2, 5, 7]. Q_{ii} is proportional to the local energy density $E_i = -\sum_j G_{ij}K_{ji}$, which is position independent in a system at thermal equilibrium. In summary, all off-diagonal elements are zero, and all diagonal elements are equivalent; thus

$$T_g = \sum_j G_{0j}K_{j0} \ , \tag{3}$$

where $i = 0$ is an arbitrary origin. The spin-freezing occurs, as any other magnetic transition, when the energy gained by ordering overcomes the loss of entropy. Hence, T_g is expected to scale with the interaction energy per spin, in accordance with Eq.(3). If in Eq.(2) we had done a MF approximation ($G_{ij} \equiv \delta_{ij}$), we would have broken the symmetry of Q_{il}. In such situations, authors have resorted to averages over different realizations of the disorder, in order to recover disorder-independent equations[3, 11]. In contrast to thermal averages, the configurational-average does not represent a physical process. The actual physical system (with quenched positional disorder) does not mutate; it remains in one configuration, yet showing sample-independent properties. Therefore, there should be an analytical approach within which T_g can be obtained from a single configuration[7, 12]; Eq.(3) is an example of such approach.

Now we split the sum in Eq.(3) into concentric shells of thickness dr, with $k_{\rm F}^{-1} \ll dr \ll \Lambda$; Λ being the range of the interaction, to be defined later. We do first the sum in every shell, since this gives us r-dependent averages, which will allow us to use the known critical behavior of the corresponding functions. As half of the bonds are frustrated[7], every shell average $\overline{G_{ij}K_{ji}}$ is equal to $(1/2)\overline{|G_{ij}||K_{ji}|}$. The positive value, which results from the correlations between the sign of $\langle S_iS_j\rangle$ and the sign of K_{ji}, is essential to the phase transition[5, 7]. We neglect the remaining in-shell correlations between the absolute values $|G_{ij}|$ and $|K_{ij}|$, and write

$$T_g \approx 2\pi c \int_{r_c}^{\Lambda} \overline{|G|}\ \ \overline{|K|}\ r^2 dr \ , \tag{4}$$

where r_c is the typical inter-spin distance, which must be proportional to, and not smaller than $(3/4\pi c)^{1/3}$. Doing so, we have not altered the r-dependence of the integrand, and therefore the resulting functional dependence on r_c and Λ remains unchanged. Although one would naively expect that, in every shell $[r; r+dr]$, larger $|G_{ij}|$s correspond to larger $|K_{ji}|$s, this is often not the case. Take as example any pair of spins for which $\cos(2k_{\rm F}r_{ij}) = 0$. The coupling K_{ji} is zero, but G_{ij} is most probably different from zero due to indirect correlations. The opposite example is also possible; $K_{ji} \neq 0$, and $G_{ij} = 0$ because of the frustration. Thus, the effect of the neglected correlations on the numerical prefactor is small. However, the uncertainty in the value of this prefactor is unavoidable, because the exact distribution of G_{ij} cannot be calculated analytically.

The critical behavior of $\overline{|G(r)|}$*:* Experiments and Montecarlo simulations[13] agree that the non-linear susceptibility $\chi_{nl} \equiv (1/N)\sum_{ij}\langle S_iS_j\rangle^2$ diverges at T_g, and that the spin-glass correlation $G_{\rm SG}(r) \equiv \overline{\langle S(r)S(0)\rangle^2}$ has a critical falloff $G_{\rm SG}(r) \propto (r_c/r)^{1+\eta}$, where η is the critical exponent. As G_{ij} is bounded (i.e., $|\langle S_iS_j\rangle| \leq 1$), the double inequality $G_{\rm SG}(r) \leq \overline{|G|} \leq \sqrt{G_{\rm SG}(r)}$ holds for any r. This implies that $\overline{|G|}$ also has an infinite range at $T = T_g$, and that

$$\overline{|G|} \propto \left(\frac{r_c}{r}\right)^{1+\eta'} \ , \tag{5}$$

with

$$-1 < \frac{\eta - 1}{2} \leq \eta' \leq \eta \ . \tag{6}$$

Whether η' is a constant (a true critical exponent) or r-dependent, is to be found by means of Montecarlo simulations. A finite cusp in the linear susceptibility at $T = T_g$ is another characteristic of spin glasses; and it implies that the correlation function $\overline{G}$ has a finite range. The long tail of $\overline{|G|}$ does not contradict this observation. $\overline{G}$ does not show a critical decay, due to the fluctuating sign of G_{ij}. The double sums $\sum_{ij}|G_{ij}|^2$ and $\sum_{ij}|G_{ij}|$ grow faster than the system size (N), whereas $\sum_{ij}G_{ij} \propto N$.

A simple equation for T_g*:* In order to test Eq.(4) with available experimental data, we take the scaling form (5) with η' as a constant, and prefactor $1/2$ (uniformly distributed correlations). For $\overline{|K|}$, we employ a simplified version for the effective RKKY interaction, due to Shegelski and Geldart[14]: a standard Ir^{-3} decay with temperature-dependent finite range $\Lambda_T \propto (T_{\rm F}\lambda/3\pi k_{\rm F}T)^{1/2} \gg \lambda$. λ, and $T_{\rm F}$ are, respectively, the mean-free-path, and Fermi temperature of the conduction electrons. $I = 9\pi J_{\rm H}^2\mu_{\rm eff}^2/T_{\rm F}(2k_{\rm F})^3$, where $J_{\rm H}$ is the s-d Hund's coupling, and $\mu_{\rm eff}$ is the effective moment of the impurity. With this, we obtain

$$T_g = \frac{\pi c I}{1+\eta'}\left\{1 - \left[\frac{r_c}{\Lambda_{T_g}}\right]^{1+\eta'}\right\} \ . \tag{7}$$

Eq.(7) can be written in terms of directly measurable quantities (c, and the resistivity of the sample ρ), taking the form

$$T_g/c = A - B\left[c^{1/6}\sqrt{\rho T_g/c}\right]^{1+\eta'} . \qquad (8)$$

Eq.(8) gives the correct behavior $T_g \propto c$, in the low concentration limit ($c \to 0$), regardless of the specific functional form of ρ. A and B are given by the following combinations of universal constants and system parameters: $B/A = [\kappa(3/4\pi)^{1/3}(3\pi n e^2/\hbar T_{\rm F})^{1/2}]^{1+\eta'}$, and $A = \pi I/(1+\eta')$. $\hbar$, and e are the Plank constant and the electron charge, respectively; n is the concentration of free electrons in the host. κ is an universal number, which accounts for our uncertainties (i) in the proportionality constant in the short length scale r_c, and (ii) in the interaction range. In reference [14], the effective interaction was calculated as $\sqrt{\overline{K^2}}$, instead of $\overline{|K|}$. The range of $\overline{|K|}$ may be slightly smaller than the range of $\sqrt{\overline{K^2}}$. Thus, we should expect $r_c/\Lambda_{T_g} = \kappa(3/4\pi c)^{1/3}(T_{\rm F}\lambda/3\pi k_{\rm F}T_g)^{-1/2}$, with $1 < \kappa \sim 10$. In the following we will show that Eq.(8) is indeed universal.

Experimental verification: We start by fitting A, κ, and η' to the data from the AuFe system, summarized by Larsen[15]. This is the only report were c, T_g, and $\rho(T_g)$ are tabulated for 17 alloys of a same family (not knowing $\rho(T_g)$, we would have to assume a model for ρ *vs* c, which would lower the quality of the fit).

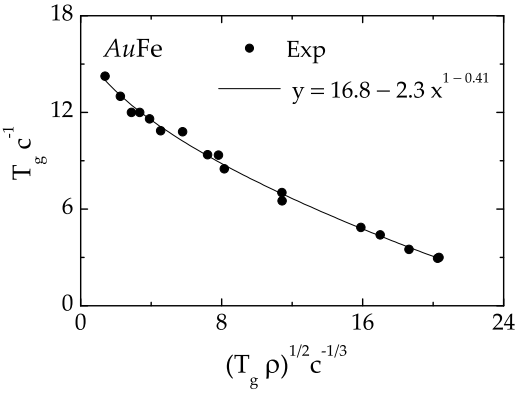

FIG. 1: The reduced freezing temperature T_g/c as a function of the damping strength in AuFe alloys. Experimental data from Ref.[15] (black dots), and theoretical fit (solid line).

In Fig.1, we show the experimental data (in black dots), together with our best theoretical fit (solid line) with $A_{\rm AuFe} = 16.8 \pm 0.8$ K/at.%Fe, $B = 2.3 \pm 0.5$, and $\eta' = -0.41 \pm 0.06$. Taking the values of the physical parameters ($T_{\rm F} = 5.5$ eV, $k_{\rm F} = 1.2\ 10^{10}$ m^{-1}, $n = 5.9\ 10^{28}$ m^{-3}, and $\mu_{\rm eff} \sim 3.25\mu_{\rm B}$), we obtain $J_{\rm H} \approx 0.3$ eV, and $\kappa \approx 10.4$. $J_{\rm H}$ falls in the expected range, and it is similar to previously reported values derived from the pressure dependence of the electrical resistivity[15]. This indicates that our approximation for the prefactor in Eq.(8) is, although not very precise, satisfactory. In order to prove the universality of Eq.(8), and that it really captures the physics of the problem, we will verify that we can reproduce the experimental data of other families of alloys, employing the values of κ and η' obtained from AuFe. To this end, we switch to the AgMn family; data from Vier and Schultz (VS)[16].

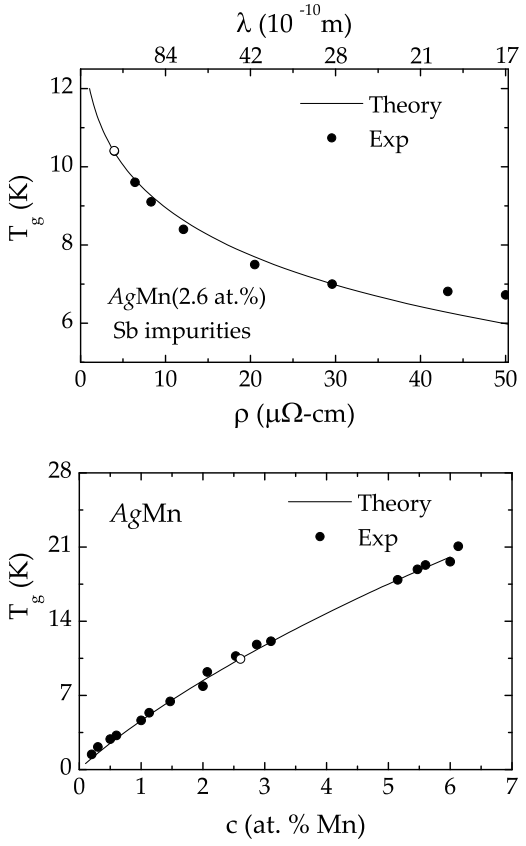

FIG. 2: The freezing temperature T_g in AgMn alloys *vs* total resistivity, with Sb impurities and 1 at.%Mn (up); *vs* concentration of Mn, and no other impurity (down). Experimental data from Ref.[16](black dots), and theoretical prediction (solid line).

The prefactor $A_{\rm AgMn} = 6.12$ K/at.%Mn is obtained from the data point ($c_0 = 2.6$ at.%Mn, $T_g = 10.4$ K and $\rho_0 = 4$ $\mu\Omega$-cm), where Mn is the only impurity, shown as an empty circle in Fig.2. Having all three parameters, we make a parameter-free prediction of T_g as a function of ρ, when non-magnetic Sb-impurities are added (upper panel), and as a function of c for clean alloys, taking $\rho = \rho_0 c/c_0$ (lower panel). The agreement between predictions and experiments is very satisfatory. Relevant deviations only appear at high ρ (λ becoming of the order $c^{-1/3}$). We should recall that the expression for the effective coupling from Ref.[14] was obtained for a weak scattering regime; i.e., low concentration of magnetic and non-magnetic impurities. The last two points in the up-

per panel correspond to more than 8 at.% of impurities (where more than 5% are non-magnetic).

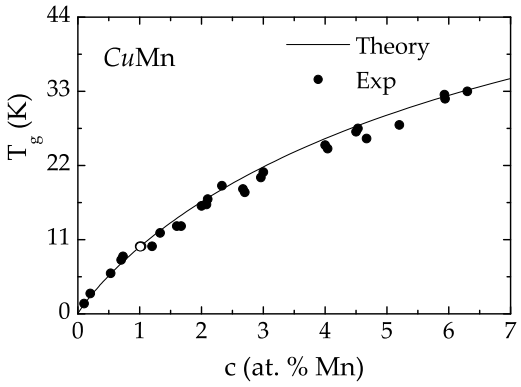

FIG. 3: The freezing temperature T_g in *Cu*Mn alloys *vs* concentration of Mn. Experimental data from Ref.[16–18](black dots), and theoretical prediction (solid line).

As a last example, we take the reports on *Cu*Mn alloys, from VS[16], (Cowen, Foiles and Shell)[17], and Mydosh et. al.[18]. The prefactor $A_{\rm CuMn}$ is fitted by forcing Eq.(8) to pass through the point ($T_g = 9.9$ K; $\rho \sim 4$ $\mu\Omega$ cm), of a clean sample *Cu*Mn(1 at.%) from Ref.[17]. This point is shown as an empty circle in Fig.3. With the obtained value of $A_{\rm CuMn} = 16.4$ K/at.%Mn, the dependence of T_g on c is predicted (solid line). Experimental data, collected from the literature, are drawn as black dots.

Summary and outlook: I have shown that $T_g \sim (1/2)\sum_{j\neq i}|G_{ij}||K_{ji}|$ gives a coherent description of the concentration-dependence of the freezing temperature in metallic spin-glasses. The sum over sites that naturally occurs in this equation, makes unnecessary the average over disorder. At the freezing point, $\overline{|G(r)|}$ has a long tail, $\propto r^{-(1+\eta')}$, with $-1 < \frac{\eta-1}{2} \leq \eta' \leq \eta$. The fit to the experimental data gives $\eta' \approx -0.41$. This seems to rule out the hypothesis of a chiral glass transition ($\eta \approx 0.6$)[19], leaving open the choice between the Ising glass ($\eta = -0.41$) and the Heisenberg glass ($\eta = -0.3$) alternatives. Studying $\overline{|G(r)|}$ by means of Montecarlo simulations and performing more measurements of $(c; T_g; \rho(T_g))$ would be of great help in finding the exact value(s) of η'. It may be also interesting to look for possible cross-overs (changes in η') as a function of the concentration and type of impurities, specially when mixing elements with different spin-orbit coupling strengths.

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